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AUTHOR(S):

Sano, Noriaki; Kawanami, Osamu; Tamon, Hajime

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Synthesis of single and multi unit-wall MgB_2 nanotubes by arc plasma in inert liquid via self-curling mechanism

Noriaki Sano,[1,a)] Osamu Kawanami,[2] and Hajime Tamon[1]
[1]*Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan*
[2]*Department of Mechanical and System Engineering, University of Hyogo, 2167 Shoha, Himeji 671-2280, Japan*

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Magnesium diboride (MgB_2) is known as a promising superconductor due to its high transmission temperature. Similarly to single-wall carbon nanotube, unique characteristics would be seen if a nanotube structure of MgB_2 having a unit-wall of Mg and B atomic bilayer is prepared. However, such MgB_2 nanotubes have not ever been synthesized. In this article, formation mechanism of unit-wall MgB_2 nanotube is elucidated by molecular mechanics calculation. From the viewpoint of energetic stability, the unit-wall will be curled up to form nanotube structure when MgB_2 crystal is disassembled to an isolated unit-wall layer. An experiment using arc plasma in inert liquid was utilized to produce unit-wall MgB_2 nanotubes. As a result, a single and multiunit-wall MgB_2 nanotube was successfully synthesized. In this reaction field, the arc plasma may play a role to produce isolated MgB_2 unit-wall fragment, and the cold cathode surface can contribute to preserve MgB_2 nanotube structure. © *2011 American Institute of Physics*. [doi:10.1063/1.3544311]

I. INTRODUCTION

Since carbon nanotubes (CNTs) were synthesized,[1,2] numerous researches about applications and theoretical aspects of CNTs have been reported because of the unique characteristics of nanotube structures.[3,4] In addition, efforts to convert various materials to nanotube structures have been made to explore novel materials which can exhibit unique characteristics. For example, titanium oxide nanotubes,[5] vanadium oxide nanotubes,[6] and molybdenum sulfide nanotubes[7] have been produced successfully as nanomaterials for photocatalytic, ferromagnetic, and lubrication applications. Such efforts have been continued not only because the various nanotubes can be used in microsize devices but also because interesting physical or chemical properties may be obtained from such structures.

Magnesium diboride (MgB_2) is one of the most attractive intermetallic superconductor because of its high transition temperature.[8–10] Nanotube structure of MgB_2 having unit-wall of Mg and B atomic bilayers can be theoretically possible because this unit-wall can be flexible like graphene sheet to construct CNT.[11] Very recently, there is a literature about synthesis of microscopic tubular MgB_2 by heating MgB_2 powders.[12] However, the tubular MgB_2 reported in this literature is substantially different from the structure theoretically predicted[11] because the body of this tubular MgB_2 is the same as bulk crystal, which has 100 nm level diameters and 30 nm level wall thickness. As a result, this tubular MgB_2 exhibits the property of bulk crystal.[12] It is well known that single-wall CNTs have many unique physical properties[3,4] which cannot be seen in multiwall CNTs, and such properties have caused the wide-spread interests by many researchers. Therefore, the synthesis of single unit-wall MgB_2 nanotubes will be essentially important to initiate the fundamental and application studies about MgB_2 nanotubes.

In this study, molecular mechanics calculation[13,14] on a fragment model is carried out to consider the formation mechanism of a unit-wall MgB_2 nanotubes. In addition, a reaction system based on arc plasma submerged in liquid[15–17] is applied to synthesize MgB_2 nanotube. In this experiment, arc plasma duration time must be carefully limited to avoid a thermal destruction of the product structures.

II. MOLECULAR MECHANICS CALCULATION

The unit cell of MgB_2 crystal is reportedly hexagonal with $a=0.3086$ nm and $c=0.3524$ nm, of which the space group is $P6/mmm$ (no. 191).[8] When MgB_2 is in crystal structure, B atoms are arranged in layers, with layers of Mg interleaved between them. The structure of B atom in each B layer is analogical to C atom in graphene layer, in which each B atom is equidistant from three other adjacent B atoms. Then, MgB_2 crystal is composed of two layers (B layer and Mg layer) stacked repeatedly along the c-axis.

The structure of each B layer in crystal phase is strongly affected by interactions from two Mg layers sandwiching this B layer. Also each Mg layer in crystal phase is affected by interactions from adjacent two B layers. Thus, if a unit wall of MgB_2 is detached from crystal phase and is kept isolated, the stable structures of each B layer and Mg layer will become different from in-crystal structures because B and Mg layers in the unit-wall layer can affect each other only on one side. This structural displacement in the layer structure may cause a stress in the unit wall, which would result in curling deformation.

In this study, fragment models of MgB_2 unit-wall are assumed for molecular mechanics calculation. An example of the models is shown in Fig. 1. In the center of this figure,

a)Electronic mail: sano@cheme.kyoto-u.ac.jp.

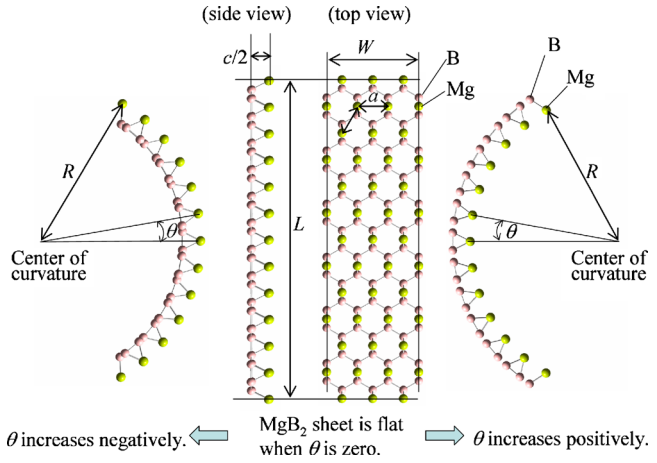

FIG. 1. (Color online) MgB_2 unit-wall fragment model for molecular mechanics calculation. The model shown here has molecular weight 2001.5 g mol^{-1}.

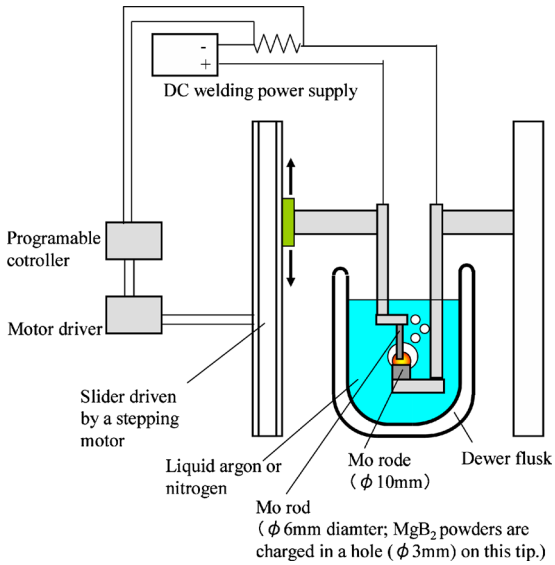

FIG. 2. (Color online) Apparatus using arc plasma in liquid to synthesize MgB_2 nanotubes. The anode motion is control by a slider driven by a stepping motor. dc welding powder supply was used to generate arc plasma between molybdenum electrodes at discharge current 120A. The arc plasma duration time is controlled by lifting the anode to break the arc discharge at a target time.

top and side views of MgB_2 unit-wall of flat structure is shown. In right and left sides in this figure, MgB_2 unit wall is curled with radius of curvature, R. The curling angle θ is defined as shown in this figure, in which θ is the angle between the lines drawn from adjacent Mg atoms commonly to the center of the curvature. When θ is positive, outside surface of this curvature is composed of B atoms while inside surface of the curvature is composed of Mg atoms. Oppositely, when θ is negative, outside surface of this curvature is composed of Mg atoms while inside one is composed of B atom. In the present model, a-spacing (distance between adjacent Mg atoms) and a half c-spacing (distance between Mg layer and B layer) are kept constant when the curvature is made. In this study, the length of the MgB_2 fragment L is changed from 1.604 nm (67atoms) to 12.293 nm (507 atoms), keeping the fragment width W constant at 0.9258 nm. In this variation, the molecular weight of the fragment model changes from 1037.2 to 7787.5 g mol^{-1}. The example fragment shown in Fig. 1 has 129 atoms, whose molecular weight is 2001.5 g mol^{-1}.

The total energies of the MgB_2 fragment models with varied θ and L were calculated by molecular mechanics calculation with Universal Force Field (UFF).[13] To carry out the calculation, a commercial software GAUSSIAN R 03W (Gaussian, Inc.) was used.

III. EXPERIMENTAL

To synthesize the unit-wall MgB_2 nanotubes, a technique using arc plasma submerged in liquid was used. This technique has been used to obtain nanotubes and related particles of carbon[15–17] and metal chalcogenides.[18] As a feature of this reaction system, stable crystals can be decomposed to fragmental species by hot arc plasma, and such species can be quenched rapidly by the effect of the hosting cold liquid. A schematic diagram of the reactor set-up used in this study is depicted in Fig. 2. To synthesize MgB_2 nanotubes, MgB_2 crystal powders (96% purity, Aldrich) were charged into a hollow molybdenum rod (outer diameter=6 mm, inner diameter=depth of the hole=3 mm) submerged in liquid, and this rod was used as an anode when arc plasma was generated. A thicker molybdenum rod (diameter=10 mm) was used as a cathode. The electrodes were connected to a direct-current welding powder supply to generate arc plasma. The MgB_2 crystals charged in the anode hole is supposed to come out through the arc plasma zone when the crystals are partially evaporated by the heat of arc plasma.

As a feature in the present synthesis of MgB_2 nanotubes distinguished from previous syntheses of other nanomaterials, liquid argon was used as an inert liquid media to avoid unnecessary byproducts. The use of such inert liquid enabled to minimize the analyses to determine the product structures. In addition, water which is often used to produce carbon nanomaterials may be too reactive[19] to synthesize the delicate nanostructures.

The location to collect the products was also unique in the synthesis of MgB_2 nanotubes. The MgB_2 nanotubes were collected from the thin film formed on the surface of the cathode tip although carbon and metal chalcogenide nanostructures were previously collected from powdery products. In addition, the control of the arc discharge duration time was also an important factor in this study. To realize this control, the anode was driven by a stepping motor slider. The arc plasma was initiated by tough-and-release way, and the interelectrode gap was kept at round 0.45 mm to continue the discharge. The anode was rapidly moved away from cathode to stop the arc plasma after a set time. In the present condition, the arc discharge current was controlled at 120 A.

IV. RESULTS AND DISCUSSION

A. Structural study on MgB_2 unit-wall by fragment model calculation

The total energies of MgB_2 fragment models calculated by the molecular mechanics calculation should be normalized for the contribution by atomic unit of MgB_2. To know

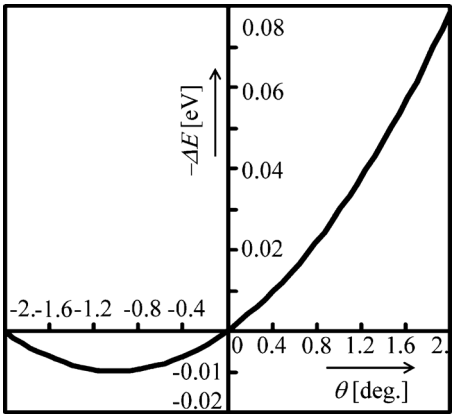

FIG. 3. Stabilization energy for curling of MgB_2 unit-wall fragment in the function of the curling angle. The curling angle θ can be referred in Fig. 1.

the stability of the curled structure of MgB_2 fragment, the energy of the flat fragment is used as a base energy. Taking these considerations into account, stabilization energy for MgB_2-layer curling is defined by Eq. (1).

$$-\Delta E = \frac{(E_\theta - E_0)}{N_{MgB_2}}. \quad (1)$$

Here, ΔE, E_θ, E_0, and N_{MgB_2} are the stabilization energy for MgB_2-layer curling contributed by atomic unit MgB_2, total energy of MgB_2 fragment model at curling angle θ, total energy of the flat MgB_2 fragment, number of atomic unit of MgB_2 existing in fragment model, respectively.

Figure 3 shows an example of the calculated results about $-\Delta E$ related with θ, which is on MgB_2 fragment model of molecular weight 7787.5 g mol^{-1}. One can see here that $-\Delta E$ can become minimum in the range of negative θ. It means that the MgB_2 unit wall tends to curl up with Mg-layer being outside surface of curvature. This tendency can be commonly observed in the calculation results on MgB_2 fragment models of other molecular weights.

The curling angle θ determined for minimum $-\Delta E$ is picked up for examined molecular weight of MgB_2 fragment models, and is plotted in the function of the molecular weight in Fig. 4. When fragment model is small, edge effect would become significant. Thus, the larger molecular weight should lead to higher accuracy. Due to the limitation of our computational power, we did not increase the molecular weight of MgB_2 fragment model to above 7787.5 g mol^{-1}. In Fig. 4, it can be seen that the curling angle θ for minimum

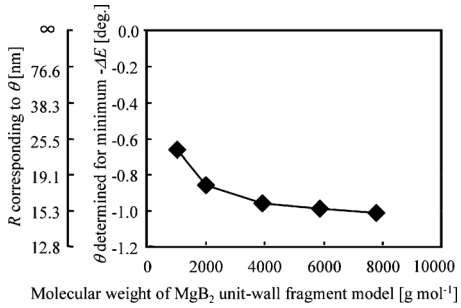

FIG. 4. Curling angle and radius of curvature of MgB_2 unit-wall fragment to minimize $-\Delta E$ at varied molecular weight of the fragment model.

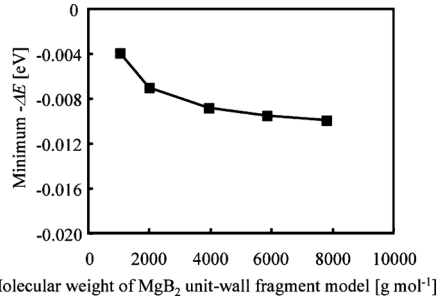

FIG. 5. Minimum $-\Delta E$ of curled MgB_2 unit-wall fragment models at varied molecular weight.

$-\Delta E$ is converged below $-1.0°$. It should be noted that θ can be geometrically related with the radius of the curvature R by Eq. (2).

$$R = \left(\frac{r_a\sqrt{3}}{2}\right)\left(\frac{180}{\theta\pi}\right). \quad (2)$$

Here r_a is distance between adjacent Mg atoms in Mg layer. A scale indicating R is added to Fig. 4 so that convergence of R with the model molecular weight can be observed. One can observe that R seems to be converged to a value below 15 nm.

Figure 5 shows the minimum $-\Delta E$ at the varied model molecular weight. In this figure, it can be seen that ΔE would be converged around 0.01 eV. For a reference to evaluate this value, the stabilization energy to stack graphene layers was calculated with the same force field using a set of two graphene fragment models, which included 504 carbon atoms.[20] In this calculation, the change in total energy of the two graphene layers from the stacked state to the isolated state was obtained to indicate the stabilization energy for graphene-layer stacking. In this calculation, a well-known in-graphite interlayer distance 0.335 nm was employed[21] for the interlayer distance in the stacked state. As a result, the stabilization energy contributed by atomic unit C for graphene-layer stacking is calculated as 0.032 eV, which is in good agreement with an experimental value 0.035 eV.[21] It should be noted that the stabilization energy for graphene-layer stacking to form graphite crystal is commonly known as a relatively weak energy among solid-composing energies. Therefore, the calculated results suggesting that the stabilization energy of MgB_2-layer curling is in the same order with that of graphene-layer stacking indicates that the thermal stability of the curling structure of MgB_2 layer is considered to be relatively low. Therefore, it can be expected that cold environment may be suitable to preserve such structure.

B. Synthesis of MgB_2 nanotube by arc plasma in liquid

Figure 6 illustrates the locations of arc plasma and the produced thin film including MgB_2 nanotubes. The arc plasma is generated with a strong light emission between the tip surface of the cathode and the edge of the hollow anode. From this arc plasma, the temperature of the anode tip is locally elevated to evaporate its edge. On the other hand, the

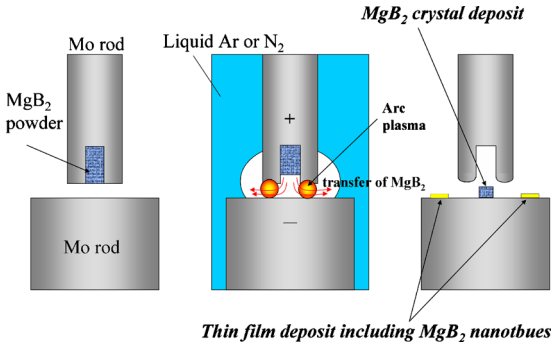

FIG. 6. (Color online) Schematic of arrangement and shapes of molybdenum electrodes, and locations of arc plasma and thin-film products. Left: Before arc discharge. Middle: Location of arc plasma between electrodes. Right: Location of products.

surface of the cathode is not consumed but stably receives thin-film products. As a result, a gray-color thin film is formed in the circumference zone around the arc plasma zone. Such film is not formed at the arc plasma zone because of excessively high temperature there. On the surface of the cathode under the anode hole, a bulky deposit of MgB_2 crystals appeared by their transfer from the anode hole. MgB_2 nanotubes were discovered in the gray-color film by observation using a transmission electron microscopy [(TEM); JEOL, JEM2010)].

Figure 7 shows a TEM image of MgB_2 nanotubes observed in the thin-film product. In this figure, single unit-wall and multiunit-wall MgB_2 nanotubes are shown, whose sizes are, respectively, as diameter=6.0 nm, length=45.7 nm and diameter=11.2 nm, length=63.0 nm. The schematic images of single and multiunit-wall MgB_2 nanotubes are also shown in this figure, in which multiunit-wall nanotube can be considered as curling up structure. In the multiunit-wall nanotube seen in the TEM image of Fig. 7, the spacing between unit-walls can be observed as 1.4 nm. This spacing is approximately one-order larger than *c*-spacing in bulk MgB_2 crystal structure. Thus, either the single unit-wall or the multiunit-wall nanotubes may exhibit the physical properties of a unit-wall of MgB_2 layer, rather than that of the crystal structure. Unlike ordinal pristine CNTs, MgB_2 nanotubes seem to be open-ended.

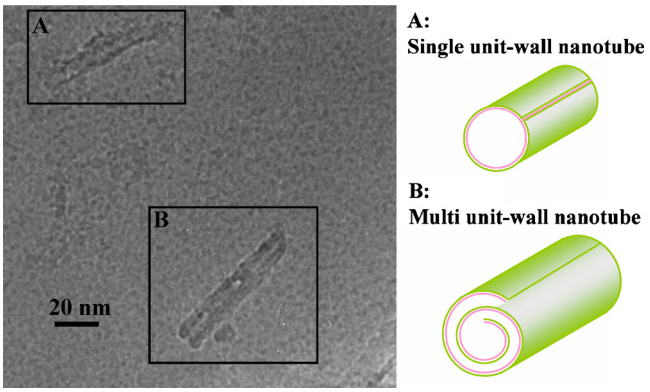

FIG. 7. (Color online) TEM image of MgB_2 nanotubes synthesized by arc plasma in liquid argon, and schematic images of single and multiunit-wall MgB_2 nanotubes. (a) and (b), respectively, show single unit-wall and multiunit-wall nanotubes.

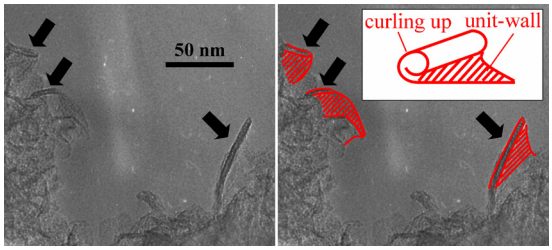

FIG. 8. (Color online) TEM image of curled edges of MgB_2 particles and schematic image of the curling.

At this stage, only TEM is used to analyze the synthesized MgB_2 nanotubes because their concentration is so low that the purification of the nanotube structure is still difficult. Nevertheless, in the reaction field of the arc plasma in liquid argon using the molybdenum electrodes charged with MgB_2 powders, the possible components in the products must be limited to Mg, B, Mo, and Ar. As a requirement to form nanotube structure, the crystal unit must be lamellar. To our best knowledge, MgB_2 is exclusively lamellar among the crystalline compounds obtainable from these components. The purification process which is necessary to proceed further analyses is currently left as future study.

The TEM observation revealed that the edges of MgB_2 crystals were highly curled in many parts of the specimen as shown in Fig. 8. The right side image of this figure shows the schematic image of the relevant curling. The isolated MgB_2 nanotubes as shown in Fig. 7 should come from the detachment of such curled edges from the main body of MgB_2 crystals. These structures obtained in the arc plasma in liquid argon were found also in the condition using liquid nitrogen.

From the discussion on the molecular mechanics calculation, it can be considered that the MgB_2 unit-wall can be curled automatically from energetic view point if the unit-wall is isolated. In the present experiment using arc plasma, unit-wall may be peeled off from MgB_2 crystals by ionic collisions, and this unit-wall can lead to the nanotube structure by the self-curling mechanism. Because the nanotube formation may occur in the narrow zone close to the cathode surface, the part of nanotube products can deposit on the cold cathode surface. It should be reminded that the thermal stability of the curled structure of MgB_2 unit-wall may be relatively low as discussed using the molecular mechanics calculation. Therefore, the cold surface of the molybdenum cathode submerged in liquid argon or in liquid nitrogen can contribute to preserve the nanotube structures consisting of curled MgB_2 unit-wall.

The radius of curvature in MgB_2 unit-wall fragment model R is equivalent to the radius of MgB_2 nanotube. Thus, R observed in TEM observations is smaller than the value obtained by molecular mechanics calculation: R obtained by molecular mechanics calculation is three to five times larger than that observed in TEM observation. Nevertheless, we consider that such order-level agreement can be considered as fair because the calculation conducted here is the first trial using simple approximations in molecular models, and importantly the self-curling mechanism of MgB_2 can be explained by the current model calculation. Improved calcula-

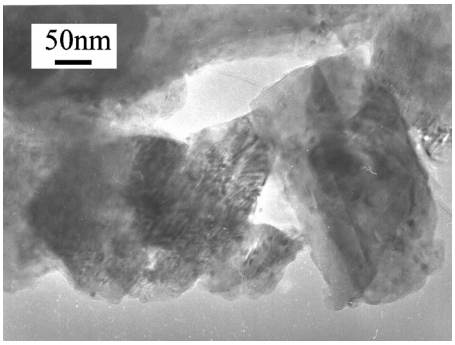

FIG. 9. TEM image of collected sample from the condition with arc plasma duration time 0.24 s. Here, curled edges and nanotube structures are not seen, and only crystalline particles are observed.

tions with varied chiral angles[3] and elaborate structural optimization to decrease the discrepancy will be conducted for further study.

It is found that the control of the arc plasma duration time is critical to obtain MgB_2 nanotube. The curled edge on MgB_2 crystals and the isolated MgB_2 nanotubes as shown in Figs. 7 and 8 were only found when the arc plasma duration time was controlled to around one second. When the arc plasma duration time is so short as 0.24 s, such structure was not observed. Instead, only MgB_2 crystals were observed as in Fig. 9. Oppositely, if the arc plasma duration time is too long, the curled edges and nanotube structures should be destroyed thermally because the temperature at the cathode surface should be elevated then. As a result, the product structure after arc plasma duration time at 1.5 s was observed as similar to Fig. 9.

The factors which determine the optimized arc discharge time to obtain MgB_2 should be considered because such time can be dependent on the experimental conditions. The time to expand the arc plasma to occupy the interelectrode zone to generate MgB_2 fragment should mainly depend on the arc discharge current, and the size and component of the electrodes. In our experiment, we consider that 0.24 s is not long enough to achieve this plasma expansion. In addition, it is required that the temperature of the cathode surface must not be above the temperature which can destroy the MgB_2 nanotube structure although the temperature of the cathode should elevate by time. The temperature elevation rate of the cathode should be also determined by the arc discharge current, and the size, and component of the electrodes. In addition, the component and flow dynamics of the liquid media should be influential on the change in the cathode temperature. In the experiments demonstrated in this study, 1.5 s was long enough to reach the cathode temperature which can destroy the MgB_2 nanotube. Because the factors mentioned here determines the effective time scale for MgB_2 nanotube synthesis, the optimized arc discharge time around one second should be shifted when one of these factors is changed.

One may wonder why MgB_2 nanotubes structure cannot be preserved in elevated temperature environment at the excessive arc discharge time although the molecular mechanics calculation can indicate that the curled structure can have minimum energy. For the answer to this question, it must be reminded that the curled structure can have the minimum energy when the MgB_2 unit layer (the combination of one Mg layer and one B layer) is kept isolated. When one Mg layer is sandwiched by two B layers, this combined layer will not be curled because of its symmetrical property. Also, when one B layer is sandwiched by two Mg layers, this combined layer will not be curled as well. Thus, each layer in MgB_2 crystal should not be curled because the bulk crystal MgB_2 consists of repeated stacking of Mg and B layers, in which all Mg and B layers are sandwiched one another except at bulk surface. When condensed solid phase of Mg and B including nanotubes are heated on the high-temperature cathode surface, the bulk crystal MgB_2 will be formed from thermal atomic motion. In this product, the MgB_2 layer is not curled as explained. On the other hand, MgB_2 nanotube can be formed when collisions between MgB_2 fragments are retarded in vaporized phase around the arc plasma zone.

V. CONCLUSIONS

The molecular mechanics calculation with UFF based on MgB_2 unit-wall fragment model was conducted to elucidate the formation mechanism of MgB_2 nanotube. As a result, self-curling mechanism of the MgB_2 unit-wall can be expected energetically. Also, it is expected that the curled structure is not so thermally strong so that cold environment would be suitable to preserve MgB_2 nanotube. An experiment using arc plasma in liquid argon or liquid nitrogen was utilized to produce MgB_2 nanotubes, and it was successful. Here, the deposit containing MgB_2 nanotube was obtained on a specific surface of the cathode. In this reaction field, the arc plasma may play a role to produce MgB_2 unit-wall fragment, and the cold cathode surface can contribute to preserve MgB_2 nanotube structure.

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